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This 6th day of September, 2004

Translator:

Hyojin Kim
Hyo-Jin Kim

(Translation)

APPLICATION FOR PATENT

Application Number : 10-2001-17298

Filing date : April 2, 2001

TITLE OF INVENTION: POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE
LITHIUM BATTERIES AND METHOD OF PREPARING SAME

APPLICANT: Samsung Display Devices Co., Ltd.
575, Sin-dong, Paldal-ku, Suwon-si, Kyungki-do
Korea

ATTORNEYS: Won-Ho Kim, Sang-Heon Lee

INVENTOR : 1) KWEON, Ho-JIN
of Seongseong-dong 508,
Cheonan-city,
Chungcheongnam-do, Korea
2) SUH, Jun-Won
of Seongseoung-dong 508,
Cheonan-city,
Chungchongnam-do, Korea
3) JUNG, Hyun-Sook
of Seongseoung-dong 508,
Cheonan-city,
Chungchongnam-do, Korea

Submitted herewith is/are an application identified above pursuant
to Article 42 of the Patent Act.

Patent Attorneys: Won-Ho Kim
Sang-Heon Lee

To the Commissioner of
the Korean Industrial Property Office

Attachment: 1. Copy application form, specification, claims,
abstract and drawings

KOREAN INDUSTRIAL PROPERTY OFFICE

This is to certify that the following application annexed hereto is a true copy from the records of the Korean Industrial Property Office.

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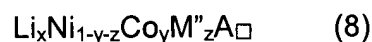
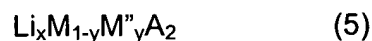
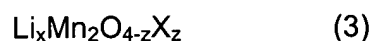
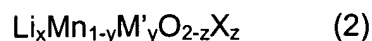
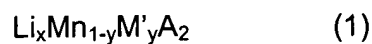
Applicant(s): Samsung Display Devices Co., Ltd.

COMMISSIONER

ABSTRACT OF THE DISCLOSURE

[Abstract]

Disclosed is a positive active material composition for a rechargeable lithium battery including a positive active material comprising at least one lithiated compound represented by formulas 1 to 9; and at least one additive compound selected from the group consisting of a metal-included hydroxide, a metal-included oxyhydroxide, a metal-included oxycarbonate, and a metal-included hydroxycarbonate.



wherein,

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 2;$$

M is one selected from the group consisting of Ni and Co;

M' is one selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr;

M'' is one selected from the group consisting of Al, Mn, Cr, Fe, Mg, Sr, V,

Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr; and

A is selected from the group consisting of O, F, S, and P.

[Representative Drawings]

5 Fig. 3

[Key words]

Positive active material, Rechargeable lithium battery, Metal hydroxide

[SPECIFICATION]

[Title of the Invention]

POSITIVE ACTIVE MATERIAL COMPOSITION FOR RECHARGEABLE LITHIUM BATTERIES

5 [BRIEF DESCRIPTION OF THE DRAWING]

FIG. 1 is a schematic drawing illustrating the process for preparing a metal hydroxide, a metal oxyhydroxide, a metal oxycarbonate, or a metal hydroxycarbonate of the present invention;

10 FIG. 2 is a graph showing XRD patterns of $\text{Al}(\text{OH})_3$ according to Example of the present invention and $\text{Al}(\text{OH})_3$ according to Reference Example, which is commercially available;

FIG. 3 is a graph showing DSC results of $\text{Al}(\text{OH})_3$ according to Example of the present invention and Al-isopropoxide;

15 FIG. 4 is a graph showing cycle-life characteristics of coin-type half-cells fabricated using positive active material compositions according to Example 1 of the present invention, Reference Examples 1 and 2, and Comparative Example 1;

20 FIG. 5 is a graph showing cycle-life characteristics of coin-type half-cells fabricated using positive active material compositions according to Comparative Example 1 and Reference Examples 3 to 5;

FIG. 6 is a graph showing XRD patterns of a $\text{HB}(\text{OH})_2$ powder according to Example 4 of the present invention and commercially available B_2O_3 ;

FIG. 7 is graph showing DSC results of HB(OH)_2 powder according to Example 4 of the present invention, H_3BO_3 , and commercially available B_2O_3 ;

FIG. 8 is a graph showing DSC results of positive electrodes prepared using active material compositions of Examples 5 and 6 of the present invention,
5 a positive electrode of Comparative Example 1, and HB(OH)_2 powder of Example 4 of the present invention;

FIG. 9 is a graph showing DSC results of positive electrodes prepared using positive active materials according to Example 8 of the present invention and Comparative Examples 1 and 2;

10 FIG. 10 is a graph showing 0.1C charge-discharge characteristic of coin-type half-cells fabricated according to Examples 5 to 6 of the present invention and Comparative Example 1;

FIG. 11 is a graph showing 1C charge-discharge characteristic of coin-type half-cells fabricated by the methods of Examples 5 to 6 of the present
15 invention and Comparative Example 1;

FIG. 12 is a graph showing cycle-life characteristic of coin-type half-cells fabricated by Comparative Example 1 and Reference Examples 1 and 2;
and

FIG. 13 is a graph showing charge-discharge characteristic of coin-type
20 half-cells fabricated by Comparative Example 1 and Reference Examples 6 and 7.

[Detailed Description of the Invention]

[Object of the Invention]

[Field of the Invention and the Related Art]

[Field of the Invention]

The present invention relates to a positive active material composition for a rechargeable lithium battery, and more particularly, to a positive active material composition for a rechargeable lithium battery having improved cycle-life and thermal-stability characteristics.

[Description of the Related Art]

Currently commercially available rechargeable lithium batteries substantially generate 4V, i.e., they have 3.7 V of average discharge potential. Such a battery is considered an essential element in the digital generation since it is an indispensable energy source for portable digital devices such as a mobile telephone, a notebook computer, a camcorder and so on, which abbreviated as 3C. For the positive active material in the rechargeable lithium battery, expensive LiCoO_2 is used in more than 95% of currently available batteries in the world market. In order to decrease costs of production, a great deal of effort is being exerted to find an alternative thereof. Although a rechargeable lithium battery using LiCoO_2 powder as a positive active material has relatively good cycle-life characteristics and good flat discharging profiles, there are still demands for improvements in electrochemical properties such as prolonged cycle-life and high power density characteristics.

As one scheme to satisfy such a demand, in U.S. Patent No. 5,292,601, Li_xMO_2 (wherein M is an element selected from Co, Ni, or Mn; x is 0.5-1) is suggested as an alternative for LiCoO_2 as a positive active material. U.S. Patent No. 5,075,291 discloses a method for fabricating a rechargeable lithiated intercalation cell including the steps of mixing a coating composition including

boron oxide, boric acid, lithium hydroxide, aluminum oxide, lithium aluminate, lithium metaborate, silicon dioxide, lithium silicate, or mixtures thereof, with a lithiated intercalation compound particulate; and fusing the coating compound at a temperature in excess of about 400°C, then coating the particulate with the fused coating compound.

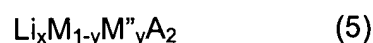
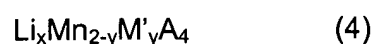
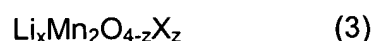
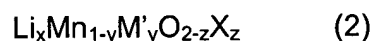
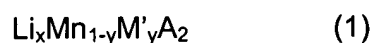
However, there is still a demand for provision of a positive active material having more improved cycle-life performance.

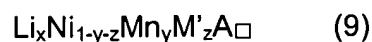
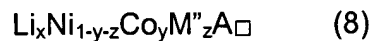
[SUBJECT MATTER OF THE INVENTION]

It is an object of the present invention to provide a positive active material composition for a rechargeable lithium battery exhibiting prolonged cycle life and high thermal-stability characteristics.

[ELEMENTS AND WORKING EXAMPLES OF THE INVENTION]

In order to achieve these objects, the present invention provides a positive active material composition for a rechargeable lithium battery including a positive active material including at least one lithiated compound represented by formulas 1 to 9; and at least one additive compound selected from a metal-included hydroxide, a metal-included oxyhydroxide, a metal-included oxycarbonate, or a metal-included hydroxycarbonate.





5 wherein,

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 2;$$

M is one selected from the group consisting of Ni and Co'

M' is one selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr;

M'' is one selected from the group consisting of Al, Mn, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr; and

A is selected from the group consisting of O, F, S, and P.

15 The present invention will be more illustrated in below.

A positive active material composition for a rechargeable lithium battery of the present invention includes a positive active material and at least one additive compound which helps to improve cycle-life characteristics and is selected from a metal-included hydroxide, a metal-included oxyhydroxide, a metal-included oxycarbonate, or a metal-included hydroxycarbonate.

20 The thermal absorbent element may include any element capable of being dissolved in an organic solvent or water, but preferably includes one

selected from Mg, Al, Co, K, Na, Ca, Si, Ti, V, Sn, Ge, Ga, B, As, or Zr.

The additive compound can be in an amorphous or crystalline form. Preferably, as shown in FIG. 1, the metal-included hydroxide, metal-included oxyhydroxide, metal-included oxycarbonate, or metal-included hydroxycarbonate may be prepared by drying an organic liquid or aqueous liquid including a metal at a range of temperature from room temperature to 200°C for 1 to 24 hours and the resulting compound has improved cycle-life.

Among the exemplary additive compounds, the metal hydroxide has the best cycle-life and thermal-stability characteristics, and further, when Al is used for the metal, amorphous Al-included hydroxide is preferable, while when B is used for the metal, crystalline B-included hydroxide is preferable.

The liquid is prepared by adding the metal or a metal-included compound to an organic solvent or water, and since the solubility of the metal varies depending upon the type of solvent, one having ordinary skill in the art can choose a suitable thermal absorbent source according to the type of solvent to be used. For example, if an organic solvent is used as the solvent, the liquid can be obtained by dissolving any of the metal, the metal-included alkoxide, the metal-included salt, or the metal-included oxide in organic solvents or by refluxing the resultant mixture. And when water is used as the solvent, the liquid can be obtained by adding only either the metal-included salt or the metal-included oxide to water or by refluxing the resultant mixture.

Examples of the organic solvent include, but are not limited to, an alcohol such as methanol, ethanol or isopropanol; or hexane, chloroform,

tetrahydrofuran, ether, methylene chloride, or acetone. The concentration of the metal in the coating liquid is not limited as long as it is capable of converting itself to the metal-included hydroxide, the metal-included oxyhydroxide, the metal-included oxycarbonate, the metal-included hydroxycarbonate, or the metal-included oxide during the drying or heat-treatment process.

The exemplary of Si-included alkoxide solution may be tetraorthosilicate which is prepared by dissolving silicate in ethanol, or the solution may also be available through commercial purchase. The exemplary of the metal aqueous solution may be vanadium oxide (V_2O_5) or ammonium vanadate ($NH_4(VO)_3$). Furthermore, the coating liquid including boron may be prepared by dissolving B_2O_3 or H_3BO_3 in an organic solvent or water, or by dissolving $HB(OH)_2$ which dissolving B_2O_3 in an organic solvent or water and drying it.

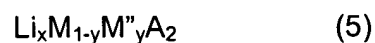
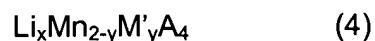
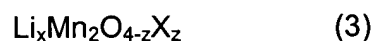
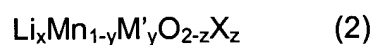
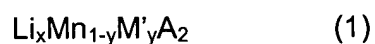
In the case when the drying process is carried out at lower than room temperature, the drying duration is unduly delayed, while it is undesirable to dry at higher than $200^\circ C$ because conversion to the desired metal hydroxide, the metal-included oxyhydroxide, the metal-included oxycarbonate, or the metal-included hydroxycarbonate becomes impossible. Further, in the case when the drying duration is shorter than 1 hour, the solvent is insufficiently evaporated, rendering a poor formation of the metal-included hydroxide, the metal-included oxyhydroxide, the metal-included oxycarbonate, or the metal-included hydroxycarbonate, while in the case of drying for longer than 20 hours, the resulting product may be broken.

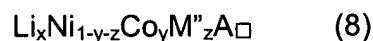
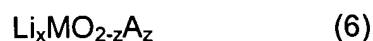
Depending on the condition of the drying process, it may be formed in

the separated form of each of the metal-included hydroxide, the metal-included oxyhydroxide, the metal-included oxycarbonate, or the metal-included hydroxycarbonate, or it may be formed in the mixed form thereof. For example, when the drying process is performed under an atmosphere of carbonate gas, metal-included oxycarbonate or metal-included hydroxycarbonate powders can be obtained.

The concentration of the additive compound of the present invention is preferable from 0.1 weight % to 1 weight %, and more preferable from 0.1 weight % to 0.5 weight % based on the weight of the positive active material composition. In the case when the concentration thereof is below 0.1 weight %, the effects of improving the cycle-life and thermal-stability characteristics to be obtained may not be sufficient. Whereas in the case when the concentration thereof is more than 1 weight %, the cycle-life characteristics are badly decreased. The present invention is advantageous since the additive compound is added in very small amounts of between 0.1 weight % and 1 weight %.

The positive active material of the present invention includes at least one lithiated compound selected from the group consisting of compounds represented by the formulas 1 to 9:





5 wherein,

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 2;$$

M is one selected from the group consisting of Ni and Co;

M' is one selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr;

M'' is one selected from the group consisting of Al, Mn, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr; and

A is selected from the group consisting of O, F, S, and P.

15 The positive active material composition may further include a binder to enhance adhesion between the positive active material composition and the current collector that is applied with the composition. Examples of the binder may include any conventional binder used in a positive active material composition, but they preferably include polyvinylidene fluoride, polyvinyl chloride, and so on. In addition, the positive active material composition may further comprise a conductor to increase the conductivity. Examples of the conductor may include any conventional conductor used in the positive active

material composition, but they preferably include a carbon.

Upon fabricating a battery with the positive active material composition in which the metal-included hydroxide, metal-included oxyhydroxide, metal-oxycarbonate, metal-hydroxycarbonate or a mixture thereof is added, the battery obtains a lot of advantages, including enhanced discharging potential, increased power, prolonged duration of use due to enlarged power characteristics compared with the same size battery, and improved thermal stability. Further, even by employing the relatively small amounts of the metal-included hydroxide, metal-included oxyhydroxide, metal-included oxycarbonate, metal-included hydroxycarbonate or a mixture thereof, the electrochemical characteristics can be dramatically enhanced.

The following examples illustrate the present invention in further detail, but the present invention is not limited by these examples.

Example 1

5g of Al-isopropoxide powder was mixed with 95g of ethanol and the resultant mixture was stirred for about 4 hours to provide a white milky Al-isopropoxide suspension. The suspension was dried in an oven at 100°C for 10 hours to obtain a white $\text{Al}(\text{OH})_3$ powder.

A LiCoO_2 powder positive active material, the resulting $\text{Al}(\text{OH})_3$ powder, a carbon conductor, and a polyvinylidene fluoride binder were mixed in the weight ratio of 93.5 : 0.5 : 3 : 3 with a N-methyl pyrrolidone solvent to obtain a positive active material slurry.

The positive active material slurry was cast in a thickness of 100 μm on

a 25 μ m thick Al foil, followed by cutting the cast foil in a circle form with a diameter of 1.6 cm to provide a coin-type positive electrode. Using the positive electrode, a fresh lithium counterpart electrode, and a 1 M LiPF₆ electrolyte solution of ethylene carbonate (EC) and dimethyl carbonate (DEC) (1: 1 volume ratio), a 2016-type coin-type half-cell was fabricated, in a glove box.

Example 2

A coin-type half-cell was fabricated by the same procedure as in Example 1, except that the weight ratio of a positive active material, an Al(OH)₃ powder, a carbon conductor, and a polyvinylidene binder was altered to 93.9 : 0.1 : 3 : 3.

Example 3

A coin-type half-cell was fabricated by the same procedure as in Example 1, except that the weight ratio of a positive active material, an Al(OH)₃ powder, a conductor, and a binder was altered to 93.1 : 0.9 : 3 : 3.

Comparative Example 1

A positive active material slurry was prepared by dissolving a LiCoO₂ positive active material, a carbon conductor, and a polyvinylidene fluoride binder in the weight ratio of 94 : 3 : 3 in N-methyl pyrrolidone solvent.

Using the prepared positive active material slurry, the coin-type half-cell was fabricated by the same procedure as in Example 1.

Reference Example 1

A coin-type half-cell was fabricated by the same procedure as in Example 1, except that the weight ratio of a positive active material, an $\text{Al}(\text{OH})_3$ powder, a carbon conductor, and a polyvinylidene fluoride binder was altered to 93 : 1 : 3 : 3.

Reference Example 2

A coin-type half-cell was fabricated by the same procedure as in Example 1, except that the weight ratio of a positive active material, an $\text{Al}(\text{OH})_3$ powder, a carbon conductor, and a polyvinylidene fluoride binder was altered to 89 : 5 : 3 : 3.

Reference Example 3

A positive active material slurry was prepared by dissolving a LiCoO_2 positive active material, an $\text{Al}(\text{OH})_3$ powder, a carbon conductor, and a polyvinylidene fluoride binder in the weight ratio of 93.5 : 0.5 : 3 : 3 in N-methyl pyrrolidone solvent. The $\text{Al}(\text{OH})_3$ powder is commercially available.

Using the prepared positive active material slurry, a coin-type half-cell was fabricated by the same procedure as in Example 1.

Reference Example 4

A coin-type half-cell was fabricated by the same procedure as in Reference Example 3, except that the weight ratio of a positive active material,

an $\text{Al}(\text{OH})_3$ powder, a carbon conductor, and a polyvinylidene fluoride binder was altered to 93 : 1 : 3 : 3.

Reference Example 5

5 A coin-type half-cell was fabricated by the same procedure as in Reference Example 3, except that the weight ratio of a positive active material, an $\text{Al}(\text{OH})_3$ powder, a carbon conductor, and a polyvinylidene fluoride binder was altered to 89 : 5 : 3 : 3.

10 FIG. 2 shows a graph illustrating XRD patterns of $\text{Al}(\text{OH})_3$ powder of Example 1 of the present invention and commercially available $\text{Al}(\text{OH})_3$ powder of Reference Example 3. As shown in FIG. 2, the $\text{Al}(\text{OH})_3$ (B of FIG. 1) powder prepared by drying the Al-isopropoxide suspension according to Example 1 is amorphous, while the commercially available $\text{Al}(\text{OH})_3$ powder (A of FIG. 1) of Reference Example 1 is crystalline.

15 FIG. 3 shows a graph illustrating DSC results of Al-isopropoxide powder and $\text{Al}(\text{OH})_3$ powder by dissolving Al-isopropoxide powder in ethanol and drying it at 100 according to Example 1. The DSC was measured using a 910 DSC (manufactured by TA Instruments). The Al-isopropoxide powder exhibited a slight endothermic reaction and a significant exothermic reaction, while the $\text{Al}(\text{OH})_3$ powder did not exhibit any exothermal phenomenon at all. Accordingly, it is anticipated that the $\text{Al}(\text{OH})_3$ powder improves thermal stability of the battery when adopted in the battery.

Further, in order to show the effects of adding the amorphous $\text{Al}(\text{OH})_3$, cycle-life characteristics were measured for coin-type half-cells fabricated according to Example 1, Reference Examples 1 and 2, and Comparative Example 1, and the results are illustrated in FIG. 4. As shown in FIG. 4, the coin-type half-cell of Example 1 (a of FIG. 3) in which $\text{Al}(\text{OH})_3$ is added to 0.5 weight % exhibits the best cycle-life characteristics, while when the amounts of $\text{Al}(\text{OH})_3$ are increased to 1 weight % (Reference Example 1, b of FIG. 3) or to 5 weight.% (Reference Example 2, c of FIG. 3), the cycle-life characteristics are similar to or even less than those when $\text{Al}(\text{OH})_3$ is not added (Comparative Example 1, d of FIG. 3).

In addition, in order to compare the cycle-life characteristics of the cell using commercial $\text{Al}(\text{OH})_3$, cycle-life characteristics were measured for coin-type half-cells fabricated according to Comparative Example 1 and Reference Examples 3 to 5, and the results are illustrated in FIG. 5. The cycle-life characteristics were measured between 4.3 V and 2.75 V by varying currents such as 0.1C 0.1 C (1 cycle), 0.2C 0.2 C (3 cycles), 0.5C 0.5 C (10 cycles), and 1C 1 C (21 cycles). As shown in FIG. 5, for the cycle-life characteristics of the cell adopting commercially available $\text{Al}(\text{OH})_3$, Reference Example 3 (b of FIG. 5) at the amount of 0.5 weight % exhibits cycle-life characteristics similar to or less than those of Comparative Example 1 (a of FIG. 5); Reference Example 4 (c of FIG. 5) at the amount of 1 weight % exhibits cycle-life characteristics less than those of Comparative Example 1; and Reference Example 5 (d of FIG. 5) at the amount of 5 weight % exhibits cycle-

life characteristics remarkably less than those of Comparative Example 1.

As shown in FIGs. 4 and 5, it was found that, using commercially available $\text{Al}(\text{OH})_3$, the cycle-life characteristics were not enhanced to the extent obtained in the present invention, and that the effects are not imparted in the case of using over 1 weight % of $\text{Al}(\text{OH})_3$.

The cells fabricated by using active materials of Examples 2 and 3 exhibit XRD, DSC, and cycle-life characteristics similar to those of Example 1.

Example 4

5g of B_2O_3 powder was mixed with 95 g of ethanol and the resultant mixture was stirred for about 1 hour to provide a 5 wt% transparent B-solution. The solution was dried at 100 for 10 hours to obtain a white $\text{HB}(\text{OH})_2$ particulate powder.

LiCoO_2 positive active material, a $\text{HB}(\text{OH})_2$ powder, a carbon conductor, and a polyvinylidene fluoride binder were mixed in the weight ratio of 93.1 : 0.9 : 3 : 3 in N-methyl pyrrolidone fluoride solvent to obtain a positive active material slurry. Using the positive active material slurry, a coin-type half-cell was fabricated by the same procedure as in Example 1.

Example 5

A coin-type half-cell was fabricated by the same procedure as in Example 4, except that the weight ratio of a LiCoO_2 positive active material, an $\text{HB}(\text{OH})_2$ powder, a carbon conductor, and a polyvinylidene fluoride binder was

altered to 93.9 : 0.1 : 3 : 3.

Example 6

5 A coin-type half-cell was fabricated by the same procedure as in Example 4, except that the weight ratio of a LiCoO_2 positive active material, an HB(OH)_2 powder, a carbon conductor, and a polyvinylidene fluoride binder was altered to 93.7 : 0.3 : 3 : 3.

Example 7

10 A coin-type half-cell was fabricated by the same procedure as in Example 4, except that the weight ratio of a LiCoO_2 positive active material, an HB(OH)_2 powder, a carbon conductor, and a polyvinylidene fluoride binder was altered to 93.5 : 0.5 : 3 : 3.

Example 8

15 A coin-type half-cell was fabricated by the same procedure as in Example 7, except that $\text{Li}_{1.03}\text{Ni}_{0.69}\text{Mn}_{0.2}\text{Co}_{0.9}\text{Al}_{0.07}\text{Mg}_{0.07}\text{O}_2$ was used as a positive active material.

Comparative Example 2

20 A coin-type half-cell was fabricated by the same procedure as in Comparative Example 1, except that $\text{Li}_{1.03}\text{Ni}_{0.69}\text{Mn}_{0.2}\text{Co}_{0.9}\text{Al}_{0.07}\text{Mg}_{0.07}\text{O}_2$ was used as a positive active material.

Reference Example 6

A coin-type half-cell was fabricated by the same procedure as in Comparative Example 1, except that the weight ratio of a positive active material, a commercially available B_2O_3 , a carbon conductor, and a polyvinylidene fluoride binder was altered to 95.7 : 0.3 : 3 : 3.

Reference Example 7

A coin-type half-cell was fabricated by the same procedure as in Comparative Example 1, except that the weight ratio of a positive active material, a commercially available B_2O_3 , a carbon conductor, and a polyvinylidene fluoride binder was altered to 94.45 : 0.55 : 3 : 3.

To confirm the structure of $HB(OH)_2$ powder prepared by the method of Example 4, XRD patterns were measured for a powder prepared according to Example 4 and the result is illustrated in a graph of FIG. 6. Furthermore, commercially available B_2O_3 (boron oxide), and the result is illustrated in a graph of FIG. 6. As shown in FIG. 6, the XRD pattern of commercially available B_2O_3 is not sharply featured, while the powder of Example 4 exhibits a single phase of XRD pattern. Since the XRD pattern of powder of Example 4 is identical to that of JCPDS Card No. 72-1067 material, it is confirmed as hydrogen borate ($HB(OH)_2$).

In addition, to show the thermal characteristics of $HB(OH)_2$ powder of Example 4, DSC was measured for a $HB(OH)_2$ powder of Example 4, commercially available H_3BO_3 (boric acid), and B_2O_3 , and the results are

illustrated in FIG. 7. As shown in FIG. 7, there are endothermic peaks for all three different powders, with each of the peaks presenting at different temperatures. Although the endothermic level of commercial H_2BO_3 is the largest, the level is presented at about 160 . As typical lithiated compounds cause exothermic reactions around 200 , the commercial H_2BO_3 cannot absorb the heat emitted from the lithiated compound so it is hard to provide a lithium battery with thermal stability with commercial H_2BO_3 . Although both $\text{HB}(\text{OH})_2$ powder and B_2O_3 exhibit endothermic reactions around 200 , the endothermic level of $\text{HB}(\text{OH})_2$ powder is more than 10 times that of B_2O_3 , so it is anticipated that $\text{HB}(\text{OH})_2$ powder gives remarkable effects of thermal stability in the lithium battery.

To find the thermal-stability effects of adding a $\text{HB}(\text{OH})_2$ powder to the positive active material slurry, DSC were measured for coin-type half-cells fabricated according to Examples 5 and 6 and Comparative Example 1, and the results are illustrated in FIG. 8. For reference, the DSC result of $\text{HB}(\text{OH})_2$ powder are illustrated in FIG. 8 (d of FIG. 8). The DSC was measured by 910 DSC (manufactured by TA Instruments) using 10 of positive active material taken from a coin-type cell that was charged to 4.3 V and disassembled in a dry room to separate the positive active material from the positive electrode. As shown in FIG. 8, $\text{HB}(\text{OH})_2$ powder (d of FIG. 8) exhibits a significant endothermic peak at around 200 , whereas pure LiCoO_2 (Comparative

Example 1, c of FIG. 8) exhibits a significant exothermic peak between 200 and 220 . This kind of exothermic reaction is caused by decomposing O_2 from the charged $Li_{1-x}Co_xO_2$ due to weakening of the Co-O linkage and reacting the generated O_2 with the electrolyte. These reactions result in degeneration of the thermal stability in the battery system. The present invention will, however, provide a battery with remarkably thermal stability by counterbalancing the exothermic reaction of $Li_{1-x}Co_xO_2$ with the endothermic reaction of $HB(OH)_2$ powder at around 200 . As shown in DSC results of Example 5 (the addition of 0.1 wt% of $HB(OH)_2$ to $LiCoO_2$, a of FIG. 8) and Example 6 (the addition of 0.3 wt% of $HB(OH)_2$ to $LiCoO_2$, b of FIG. 8), it is proven by that the exothermic peaks disappear at around 200 . As shown in FIG 8, upon increasing the adding amounts of $HB(OH)_2$ powder, the exothermic peak is moved to the higher temperature.

To show the improved effects of thermal stability by adding a $HB(OH)_2$ powder to $Li_{1.03}Ni_{0.69}Mn_{0.2}Co_{0.9}Al_{0.07}Mg_{0.07}O_2$, DSC are measured for coin-type cells fabricated by Examples 8 and Comparative Example 2, and the results are illustrated in FIG. 9. In FIG. 9, a indicates the DSC result of Example 8 and c indicates the DSC result if Comparative Example 2. In addition, the DSC result of Comparative Example 1 in which $LiCoO_2$ is adopted as a positive active material is represented in FIG. 9 (b of FIG. b), for reference. The DSC was measured by 910 DSC (manufactured by TA Instruments) using 10 of positive active material that was taken from a coin-type cell charged to 4.3 V

and disassembled in a dry room to separate the positive active material from the positive electrode. Generally, $\text{Li}_{1.03}\text{Ni}_{0.69}\text{Mn}_{0.2}\text{Co}_{0.9}\text{Al}_{0.07}\text{Mg}_{0.07}\text{O}_2$ (c of FIG. 9) has an advantage of a narrow exothermic peak and a thermal decomposition temperature higher than that of LiCoO_2 , but it also has a disadvantage of poor thermal stability since the exothermic peak is very sharp so as to suddenly emit the exothermic heat. As shown in FIG. 9, by adding HB(OH)_2 powder to the positive active material, the peak thereof becomes very broad, and the exothermic level (peak's area) is reduced (a of FIG. 9) so that the thermal stability is improved compared to that of LiCoO_2 (c of FIG. 9).

FIGs. 10 and 11 show capabilities of Examples 5, 6, and 7 and Comparative Example 1 at a low rate (0.1C) and at a high rate (1.0 C), respectively. In FIGs. 10 and 11, d indicates the capabilities of Comparative Example 1, a indicates that of Example 5, b indicates that of Example 6, and c indicates that of Example 7. FIG. 12 shows a graph illustrating cycle-life characteristics according to the charge and discharge rates in the coin-type cells of Examples 5, 6, and 7, and Comparative Example 1. In FIG. 12, a indicates the cycle-life characteristics of Example 5, b indicates that of Example 7, c indicates that of Example 6, and d indicates that of Comparative Example 1. As shown in FIGs. 10 to 12, although the capability and cycle-life characteristics are improved by adding HB(OH)_2 powder to the positive active material, the capability and cycle-life characteristics are degenerated at a high rate upon increasing the adding amount of HB(OH)_2 . Therefore, the capability and cycle-life characteristics are dramatically decreased by adding more than 1 weight % of HB(OH)_2 powder. It is found that the thermal stability is remarkably

improved by adding HB(OH)_2 powder in even a small amount. Within the range of up to 0.5 weight %, the degeneration of electrochemical characteristics is limited to the minimum. Considering the current trends concerning safety, HB(OH)_2 powder will draw a great deal of interest from the market. Further, as shown in FIG. 12, the capability characteristics are degenerated upon adding commercial B_2O_3 to the positive active material.

Further, to find the improved effects of capability characteristics by adding commercial B_2O_3 , capability characteristics at a low rate (0.1 C) were measured for coin-type half-cells fabricated by the methods of Comparative Examples 1 (LiCoO_2) and Reference Examples 6 (the addition of 0.3 w% of B_2O_3 to LiCoO_2) and 7 (the addition of 0.55 wt% of B_2O_3 to LiCoO_2), and the results are illustrated in FIG.13. In FIG. 13, a indicates the capabilities of Reference Example 6, b indicates that of Reference Example 7, and c indicates that of Comparative Example 1. As shown in FIG. 13, by adding even small amounts of commercial B_2O_3 , the capability characteristics are degenerated even less than those of bare LiCoO_2 .

[Effect of the present invention]

As mentioned above, the positive active material composition for the rechargeable lithium battery of the present invention includes a thermal absorbent element-included hydroxide, a thermal absorbent element-included oxyhydroxide, a thermal absorbent element-included oxycarbonate, or a thermal absorbent element-included hydroxycarbonate, so that the resultant battery has been improved in cycle-life and thermal-stability characteristics.

While the present invention has been described in detail with reference

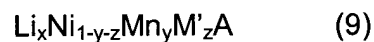
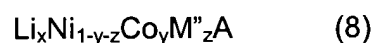
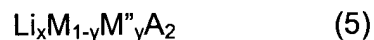
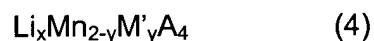
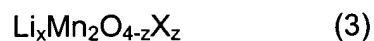
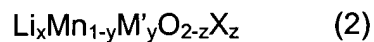
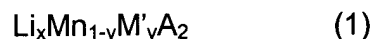
to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A positive active material composition for a rechargeable lithium battery comprising:

a positive active material comprising at least one lithiated compound represented by formulas 1 to 9; and

at least one additive compound selected from the group consisting of a metal-included hydroxide, a metal-included oxyhydroxide, a metal-included oxycarbonate, and a metal-included hydroxycarbonate.



wherein,

$$0.95 \leq x \leq 1.1, 0 \leq y \leq 0.5, 0 \leq z \leq 2;$$

M is one selected from the group consisting of Ni and Co'

M' is one selected from the group consisting of Al, Ni, Co, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th,

Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr;

M" is one selected from the group consisting of Al, Mn, Cr, Fe, Mg, Sr, V, Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr; and

5 A is selected from the group consisting of O, F, S, and P.

2. The positive active material composition according to claim 1, wherein the metal is selected from the group consisting of Mg, Al, Co, K, Na, Ca, Si, Ti, Sn, V, Ge, Ga, B, As, and Zr.

3. The positive active material composition according to claim 1,
10 wherein the additive compound is presented from 0.1 weight % to 1 weight % based on the weight of the positive active material composition.

4. The positive active material composition according to claim 1, wherein the additive compound is prepared by drying a liquid comprising a metal or a metal-included compound at a temperature ranging from room
15 temperature to 200 for 1 to 24 hours.

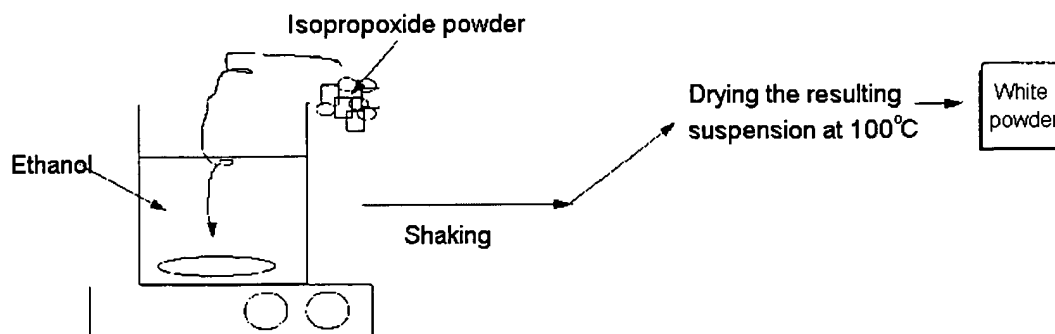


FIG. 2

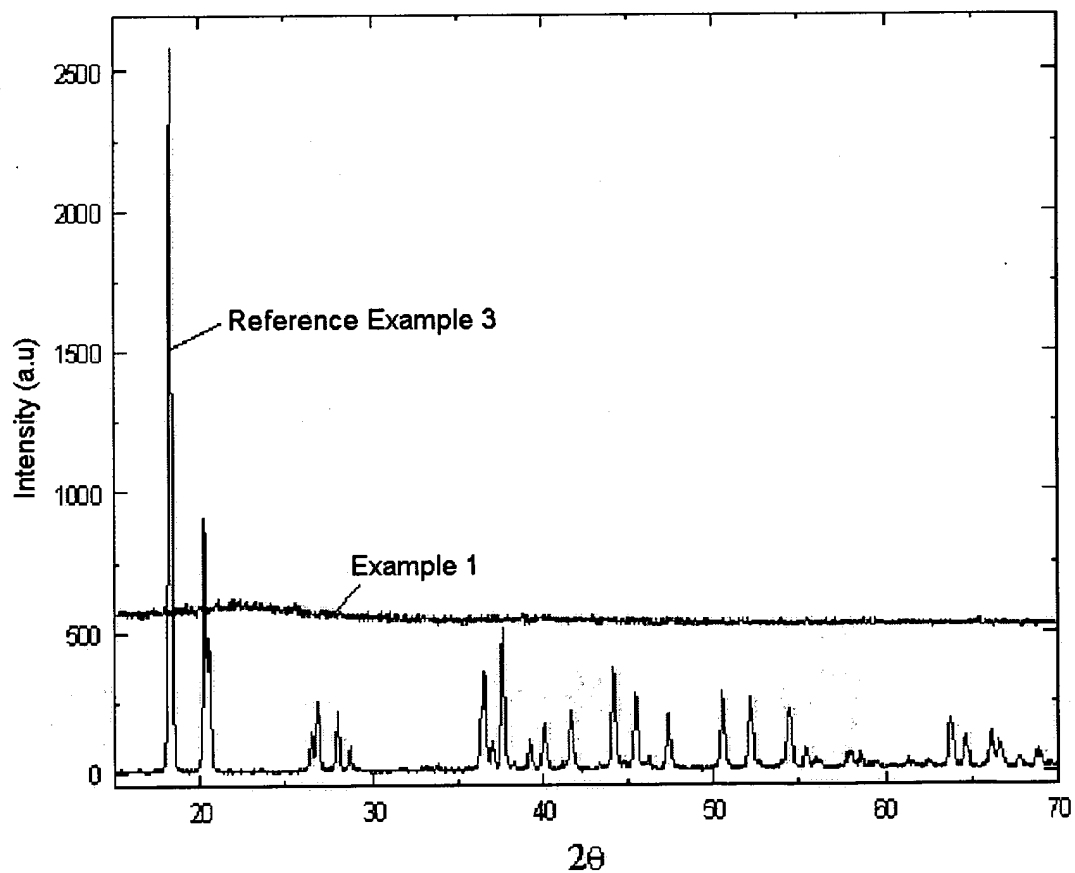


FIG. 3

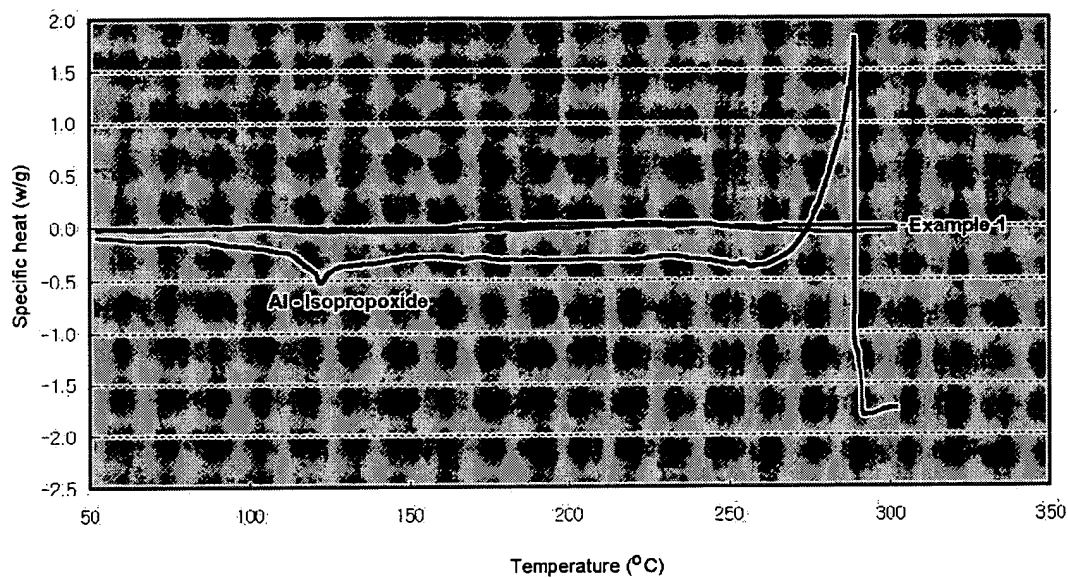


FIG. 4

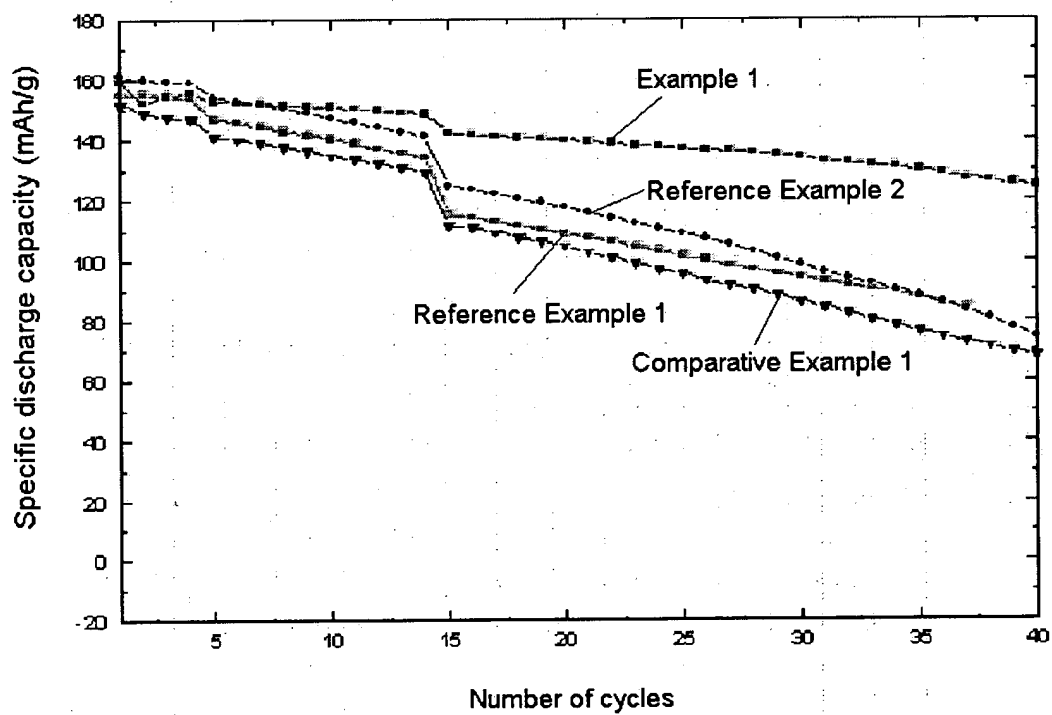


FIG. 5

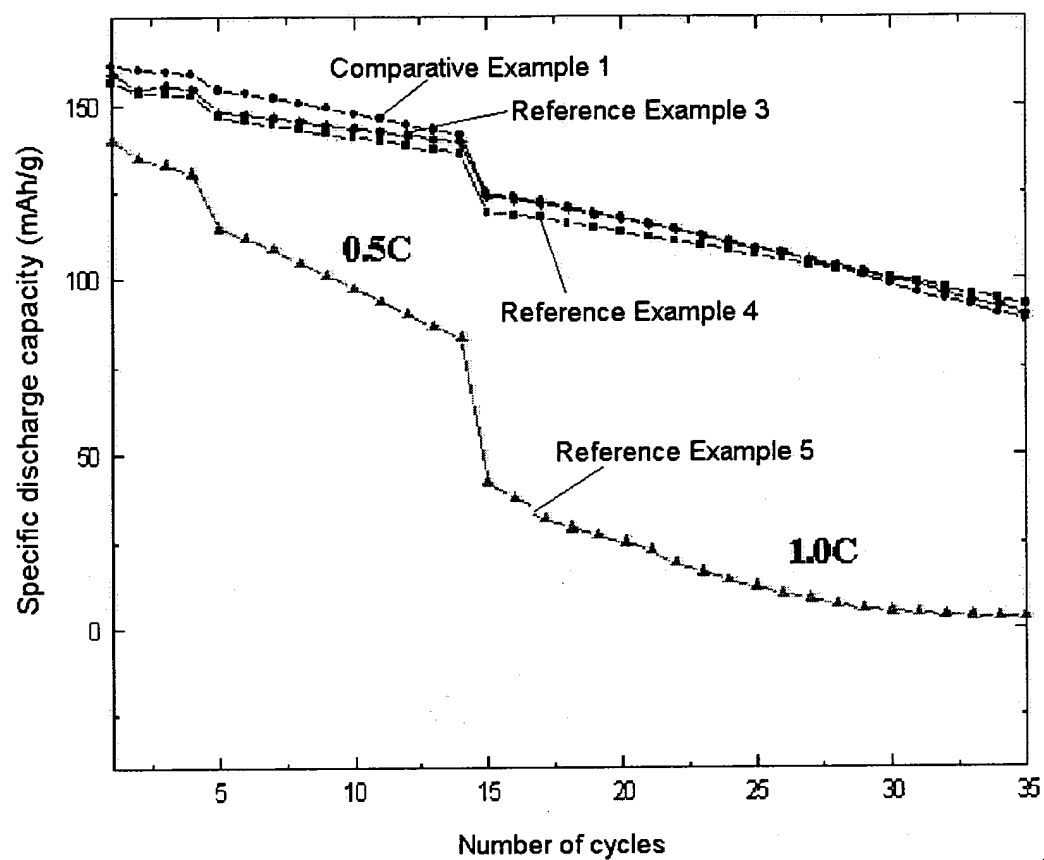
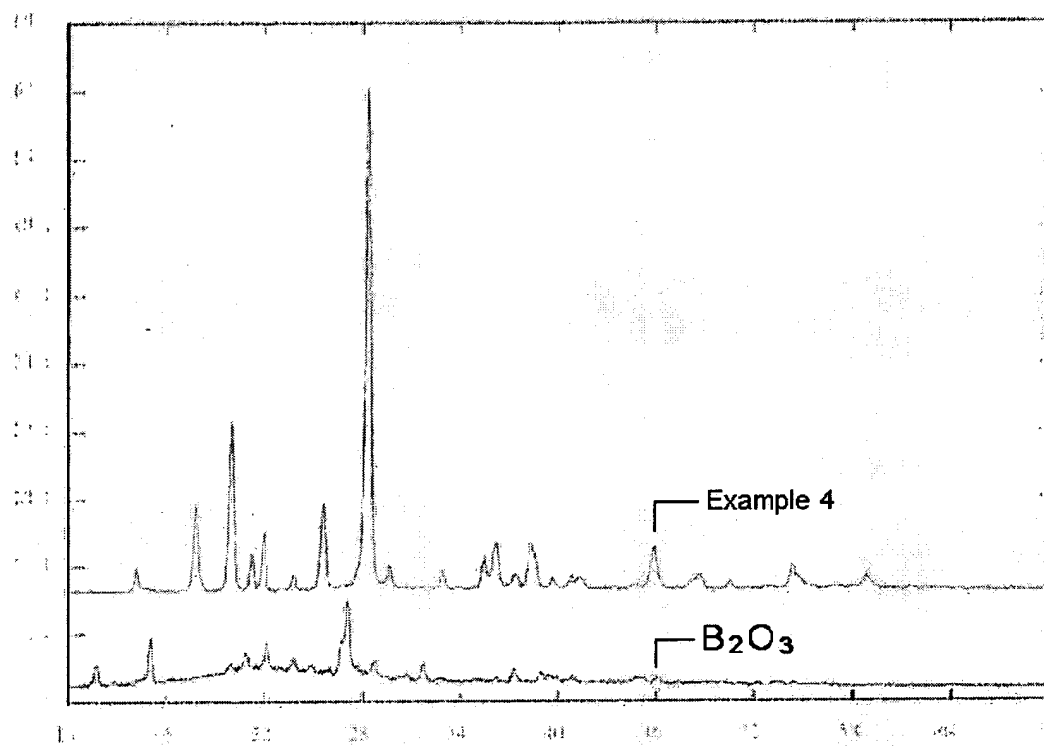


FIG. 6

B : B₂O₃, R : R₂O₃



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FIG. 7

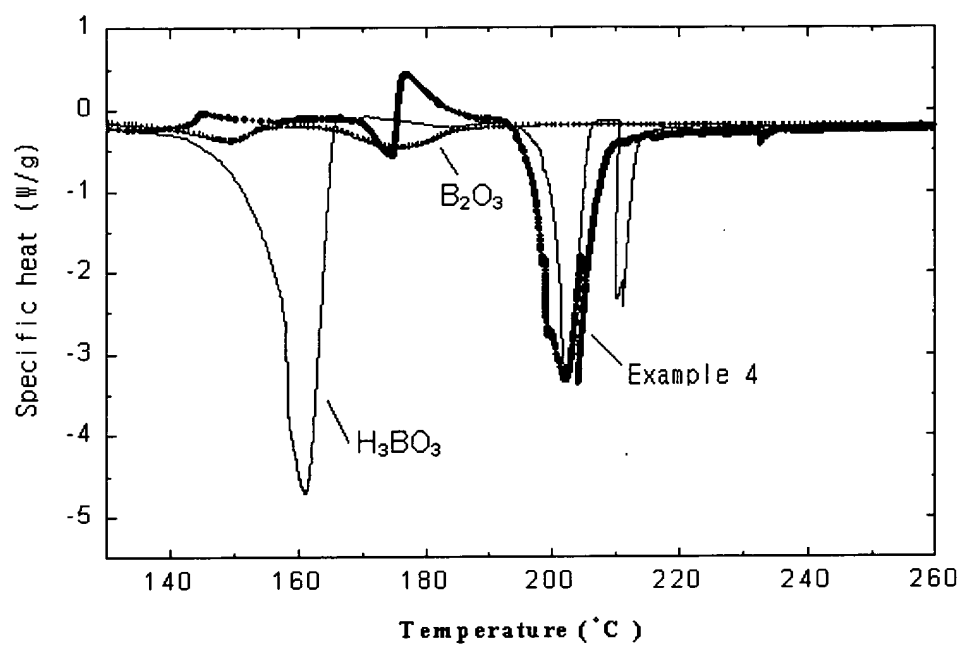


FIG. 8

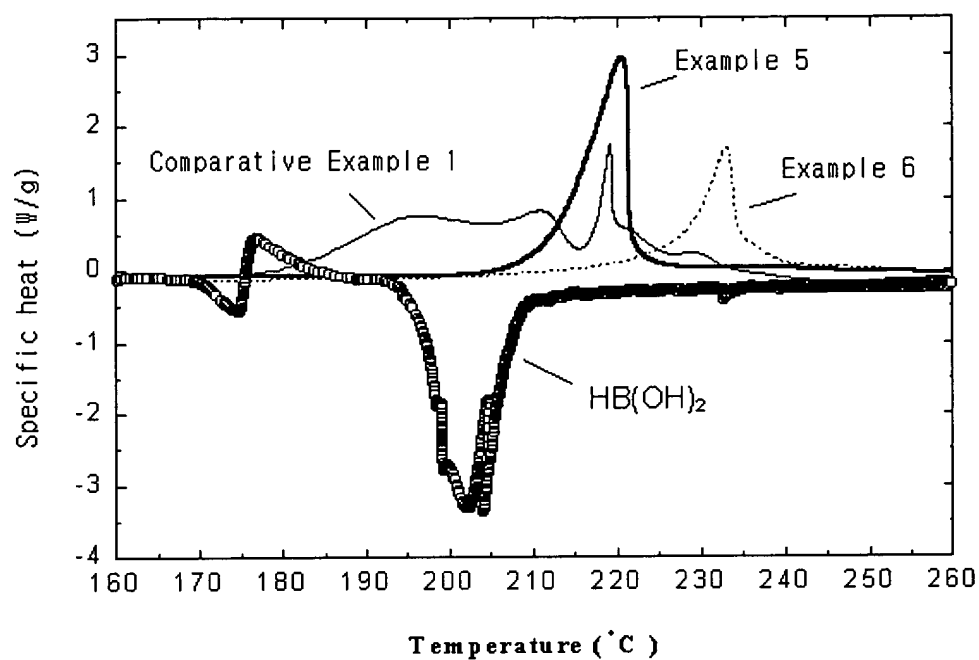


FIG. 9

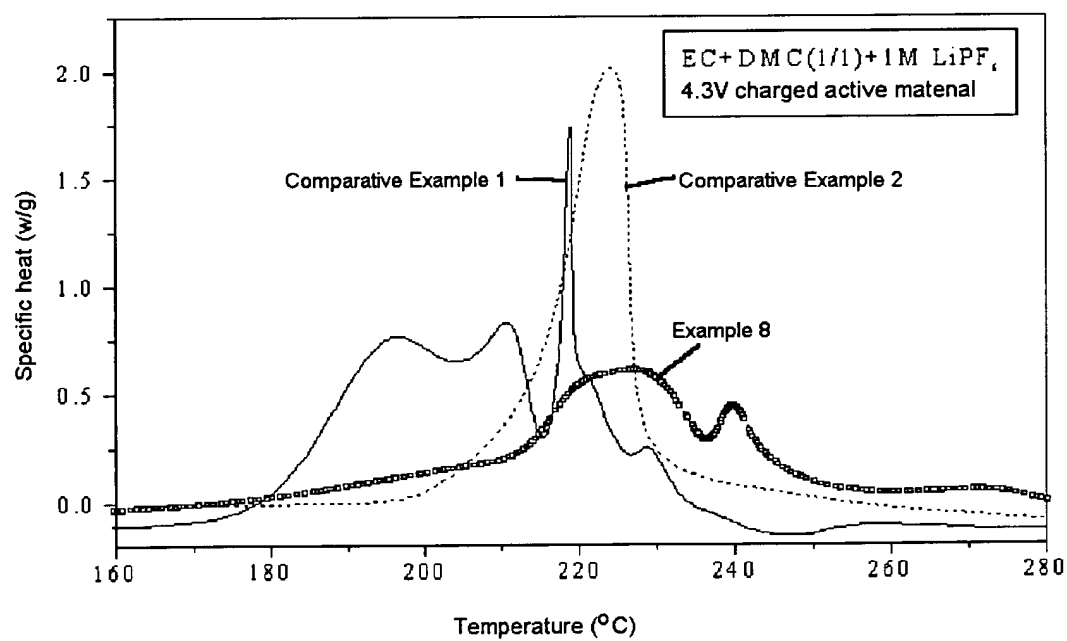
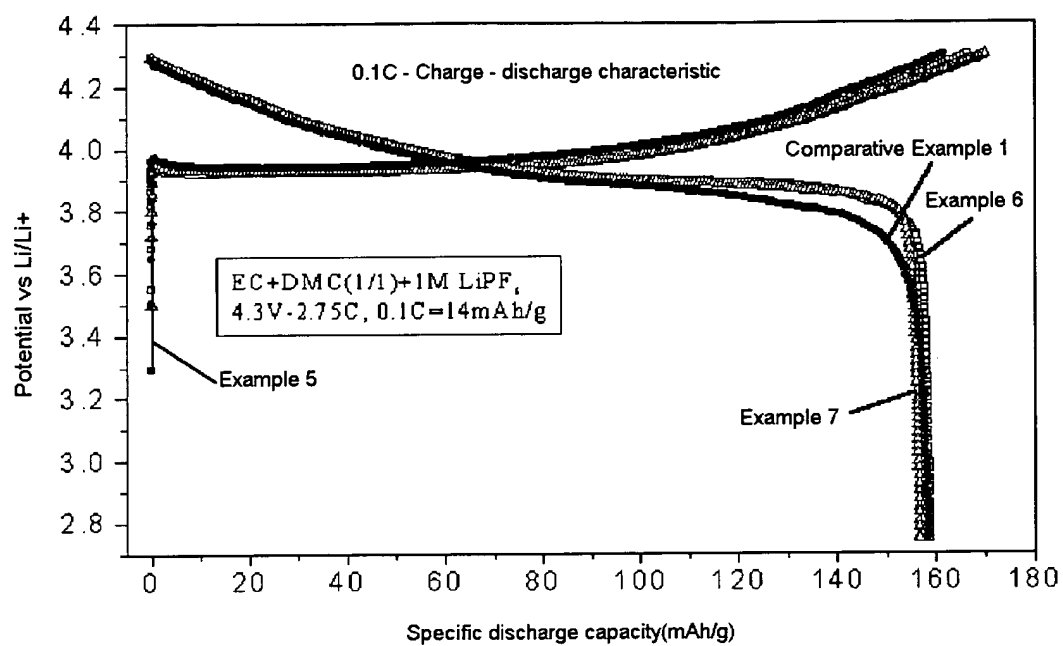


FIG. 10



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FIG. 11

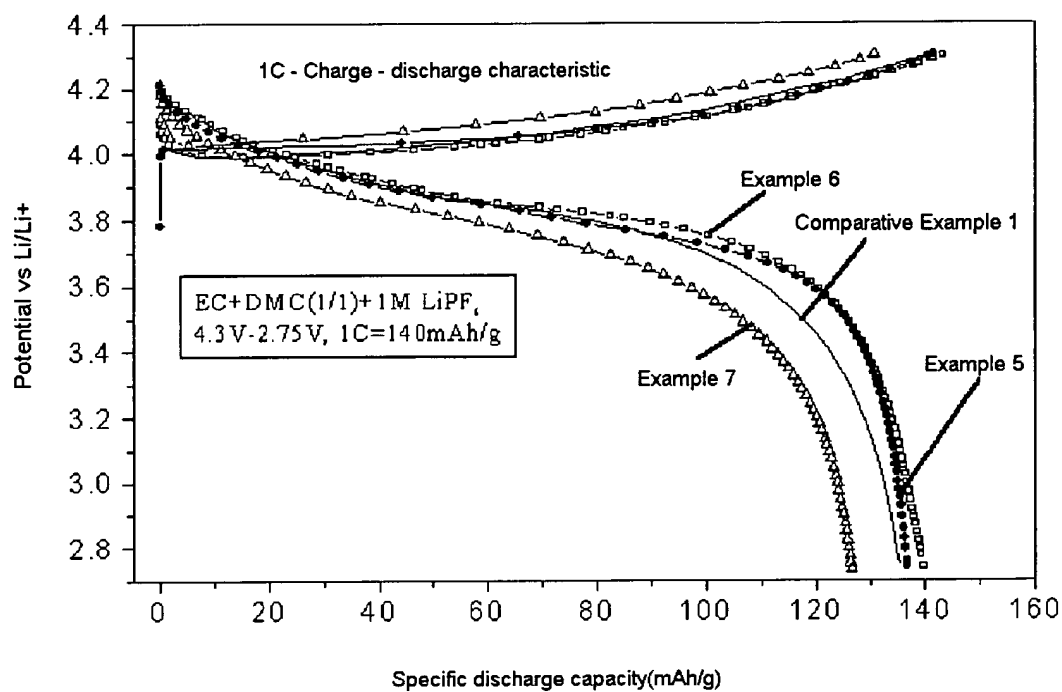


FIG. 12

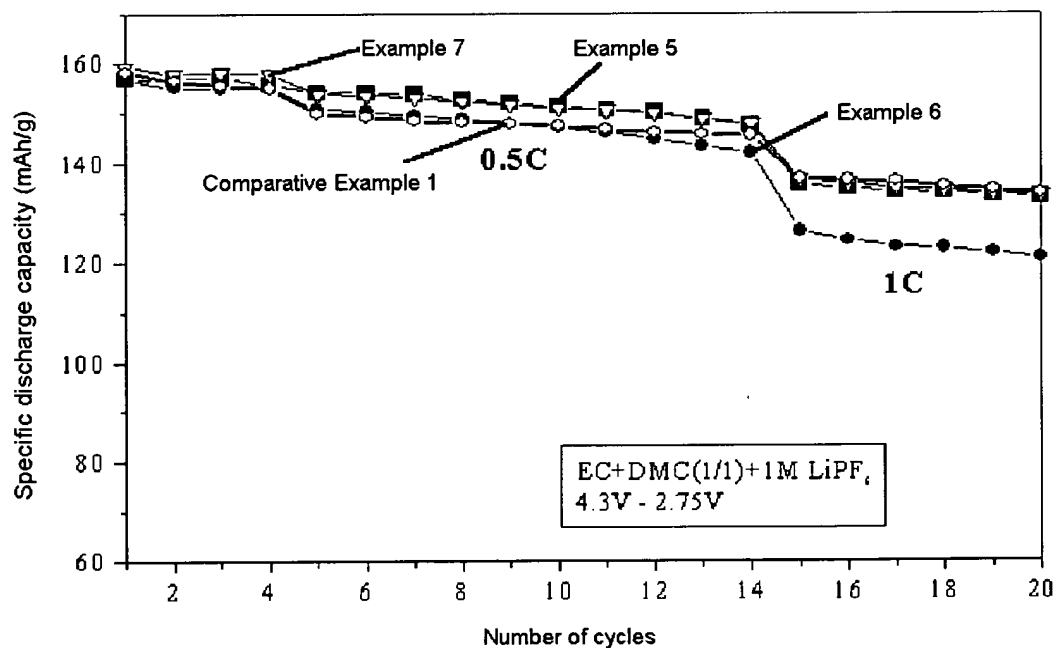


FIG. 13

